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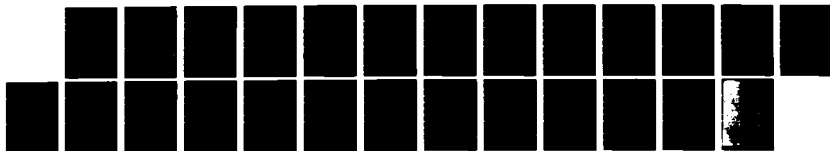
THE EFFECT OF PLASTICIZER ON THE PIEZOELECTRIC
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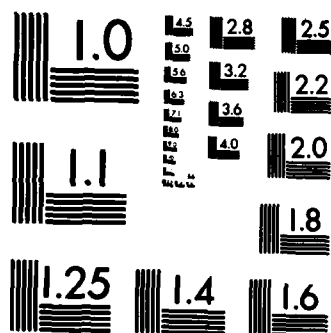
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Technical Report No. 2

THE EFFECT OF PLASTICIZER ON THE PIEZOELECTRIC
PROPERTIES OF UNORIENTED POLYVINYLIDENE FLUORIDE FILMS

by

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ABSTRACT

The effect of plasticizer content on the piezoelectric response of unoriented polyvinylidene fluoride was measured. The plasticizer was added both before and after poling. In both cases the piezoelectric strain constant d_{31} increased appreciably with increasing plasticizer content. When the plasticizer was added before poling the piezoelectric stress constant e_{31} also increased with plasticizer content. The reverse effect was observed for e_{31} if the plasticizer was added after poling (probably due to film depolarization). These changes in d_{31} and e_{31} are related to the bulk mechanical and dielectric properties of the plasticized films.

Introduction

Studies of the piezoelectric properties of polymer films in recent years have tended to emphasize the role of the crystalline component. For polyvinylidene fluoride it has been established that residual polarization after poling arises from dipole orientation in the crystalline regions, which (for the phase I and phase IV crystal form) occurs by a ferroelectric switching mechanism¹⁻³, or (for the non-polar crystal form phase II) occurs by non-polar to polar crystal phase transitions⁴⁻⁶. It has been shown that the crystal orientation with respect to the applied field is important both to the poling mechanisms possible and to resulting piezoelectric stress and strain constants (e_{31} and d_{31}) of the films⁶. Other studies have been concerned with the Curie temperatures of the crystals.

However a number of other experiments have suggested that the magnitude of the piezoelectric and pyroelectric response also depends on transitions in the amorphous region⁷⁻¹⁰. In a recent study, the pressure dependence of the piezoelectric hydrostatic pressure coefficient d_p and the pyroelectric coefficient p_y was determined from atmospheric pressure to 7 Kbar over a temperature range from -80°C to $+48^\circ\text{C}$ for poled uniaxially oriented films⁸. The effect of the glass transition on d_p and p_y as a function of pressure was marked and consistent over a wide range of pressure and temperature. Similar behavior was observed for unoriented films⁹. A study by J.I. Scheinbeim¹¹ of the effect of temperature on the piezoelectric strain constant d_{31} of poled nylon 11 films suggested that the glass transition affected the magnitude of the piezoelectric response for this polymer also. Finally, a study of the effect of water on poled nylon 11 films suggested that water acted as a plasticizer and changed the measured values of d_{31} and e_{31} for these films¹².

The piezoelectric and pyroelectric properties of poled crystalline polymer films are likely to be greatly influenced by the amorphous component for two

reasons. First, it should be noted that changes in charge density on the film electrodes arise from changes in dipole density per unit volume in the film, and these depend on the bulk compressibility and thermal expansion as well as on the crystal compressibility and thermal expansion. This is made explicit in the treatment of Broadhurst, Davis and McKinney¹³. Second, changes in the total dipole moment for a crystal are coupled to the electrodes through a semicrystalline medium. The apparent dipole moment, external to the crystal, depends on both bulk dielectric constant and crystal dielectric constant as well as on crystal morphology and size, and also bulk conductivity.¹³.

For these reasons, it seemed appropriate to explore the role of the amorphous component in the piezoelectric response of PVF₂ films by the use of plasticizer compounds. Since, the use of plasticizers can cause changes in crystal orientation, in this study only unoriented films were used. The results of other investigations of oriented PVF₂ films and nylon 11 films are published separately.

Experimental

Kureha capacitor grade biaxially oriented films were heated to 210°C between aluminum foils and then crystallized by slow cooling to room temperature to produce unoriented films with uniform thickness. The plasticizer used was tricresyl phosphate (80% para, 20% meta). A thin layer of aluminum was evaporated onto the films to serve as electrodes. All the films were poled in a vacuum (10^{-6} torr) using a device which automatically ramped voltage at a constant rate to the maximum voltage and held at this poling field for 10 minutes (poling time).

Two experiments were carried out;

(a) the films were poled first using a poling field of 1.0×10^6 V/cm, and a poling temperature of 70°C and then plasticizer added by immersion in the liquid plasticizer at 63°-65°C for various times (dipping times).

(b) the films were plasticized before poling by immersion in the

plasticizer at various temperatures (dipping temperature) for various times, and then poled.

Results and Discussion

Figure 1 shows the piezoelectric strain constant d_{31} of the poled unoriented films which were subsequently plasticized. The same sample was used to obtain all these data, the dipping time accumulating by repeated immersion in the plasticizer following measurement of d_{31} . The absolute magnitude of d_{31} is not large for any of these films because the slow crystallization from the melt yields the non-polar phase II crystal form. Previous studies have shown that residual polarization in these films arises from field-induced crystal phase transitions to polar phases, depending on poling field and crystallite orientation⁶. Figure 1 shows that the piezoelectric strain constant d_{31} increases with increased absorption of plasticizer until a value approximately 25% higher than the initial value of the unplasticized film is reached. Further immersion of the poled films in plasticizer under these conditions did not appear to further increase d_{31} . The dipping temperature (63-65°C) was chosen as a compromise, lower than the poling temperature (75°C) and high enough to ensure adequate diffusion of plasticizer into the film.

Figure 2 shows the measured values of the piezoelectric stress constant e_{31} for the same films. The measured value of e_{31} decreases steadily with increasing plasticizer content up to a maximum loss of about 20%. This data suggests that despite the higher values of d_{31} measured some depolarization was caused by immersion in the plasticizer.

Figures 3 and 4 show the measured values of the dielectric constant and the elastic modulus for the same films. The increasing dielectric constant and the decreasing modulus reflect the increased plasticizer content.

The piezoelectric strain constant is defined as the rate of change of bulk

polarization with stress (applied in the plane of the film) or

$$d_{31} = (dP/d\sigma)_{\epsilon, T},$$

while the piezoelectric stress constant is defined as the rate of change of bulk polarization with strain or

$$e_{31} = (dP/d\epsilon)_{\sigma, T}.$$

From the definition it follows that

$$E = e_{31}/d_{31}$$

where E is the elastic modulus. Since all these three constants have been measured, this ratio was checked for all data and found to be within experimental error.

In the interpretation of these results, it is important to remember that the piezoelectric constants are related to the rate of change of polarization with either stress or strain. For the d_{31} constant, the application of stress in the plane of the film causes a reduction in thickness of the film (depending on Poisson's ratio) and a consequent increase in polarization. We do not know how Poisson's ratio changes with plasticizer content. However, increasing plasticizer content decreases the elastic modulus, as seen in Figure 4, and so greater reductions in film thickness should occur at the same stress level, if the Poisson ratio does not change appreciably. For this reason, an increase in d_{31} with plasticizer content can be understood.

The e_{31} coefficient changes in bulk polarization with respect to strains in the plane of the film are measured. For the same levels of strain in the plane of the film, if Poisson's ratio does not change appreciably, reductions in film

thickness will be the same (independent of modulus) and we might expect ϵ_{31} to be constant with plasticizer content on these grounds. The observed decrease in ϵ_{31} might be attributed to a decrease in total polarization of the film resulting from immersion in the plasticizer at the elevated temperatures. If this is true, the observed increase in d_{31} despite this decrease in total polarization is even more striking.

Figures 5, 6, 7, and 8 compare unplasticized films with films plasticized before poling. All the plasticized films were plasticized by immersion in tricresyl phosphate at 100°C for eight hours. All the films were subsequently poled at 22°C, with a poling time of ten minutes and various poling temperatures. The films could now be immersed in tricresyl phosphate at a higher temperature, since no loss in polarization resulting from these temperatures could ensue.

Figure 5 compares the resulting d_{31} coefficients for plasticized and unplasticized films, for films poled at various fields from 0.5×10^6 V/cm to 1.75×10^6 V/cm. The plasticized films all have higher d_{31} values, the increase being in the range of 30-50% depending on poling field, but being higher for the lower poling fields.

Figure 6 compares the resulting ϵ_{31} coefficients for the same plasticized and unplasticized films. When the plasticizing step is carried out prior to poling, the ϵ_{31} values for the plasticized films are also higher than for the unplasticized films, the increase being greater for films poled at the highest fields. Figures 7 and 8 compare the dielectric constants and elastic moduli of the plasticized and unplasticized films. As expected, these values do not change with poling field. The modulus of the plasticized films is ~20% lower than the modulus of the unplasticized films and this accounts for the higher d_{31} values of the plasticized films.

The higher ϵ_{31} values for the plasticized films cannot be accounted for in this way. Two possibilities are suggested. First, the total polarization

following poling may be greater for the plasticized films, the higher mobility in the plasticized amorphous regions under field, enabling the phase II crystals to transform to polar crystals to a greater extent. Second, the higher dielectric constant of the plasticized films may enable changes in crystal polarization to be coupled to the film electrodes more efficiently. Broadhurst, Davis and McKinney¹³ point out that for infinitely thin crystals, no field due to crystal dipole moment is internal to the crystal and suggest that the morphology of semicrystalline polymers (very thin lamellae) might be likely to approximate this situation. The morphology of polyvinylidene fluoride however has not been investigated in detail and the validity of this assumption remains unknown at this time. For crystals of finite size, the apparent moment of the crystal will depend on the dielectric constants of both crystal and amorphous regions, and on crystal shape. In general for finite crystals the apparent crystal moment will increase with the bulk dielectric constant (and hence with plasticizer content).

Figure 9 shows the d_{31} constants for films plasticized by immersion in plasticizer at different temperatures (dipping temperatures) for eight hours prior to poling. Presumably, the adsorption of plasticizer by the film is greater at higher temperatures. We observe that d_{31} increases with plasticizer content up to ~30% relative to the unplasticized film, and then at even higher plasticizer contents (dipping temperatures -120°C and 140°C) declines slightly. X-ray diffraction scans of the films plasticized at these higher temperatures revealed that the crystallinity of those samples has decreased greatly (to ~25-30%), due to partial dissolution of small crystals. This suggests that the total polarization of the plasticized films is not greater than the unplasticized films and is probably considerably less at the higher plasticizer content due to reduced crystallinity.

Figure 10 shows the e_{31} constants for the same films while Figures 11 and 12 show the corresponding values of modulus and dielectric constant. e_{31} shows a

similar variation with dipping temperature as d_{31} . While the modulus decreases steadily with dipping temperature, the dielectric constants of the plasticized films shows a similar variation to d_{31} and e_{31} . While the reason for the small decrease in dielectric constant at the higher dipping temperatures is not apparent, it appears that d_{31} and e_{31} are sensitive to this effect.

Further studies to determine the change in Poisson's ratio with plasticizers content, and to directly measure the plasticizer content are presently being carried out.

Conclusions

We conclude that the piezoelectric and pyroelectric stress and strain constants e_{31} and d_{31} are sensitive to the bulk mechanical and dielectric properties of the films. Since these properties are greatly influenced by the amorphous regions for a semi-crystalline polymer, the state of the amorphous content is important to the measured piezoelectric response of poled films. We expected d_{31} to increase with increased film compliance and this was observed. An increase in e_{31} was also observed and this appeared to be related to dielectric constant. We speculate that this affect arises from the reduction of the coupling of changes in crystal polarization to the electrodes on the film surface.

Changes in the mechanical and dielectric properties of films can be induced by changes in plasticizer content and thus the piezoelectric response of poled films can be varied by varying plasticizer content.

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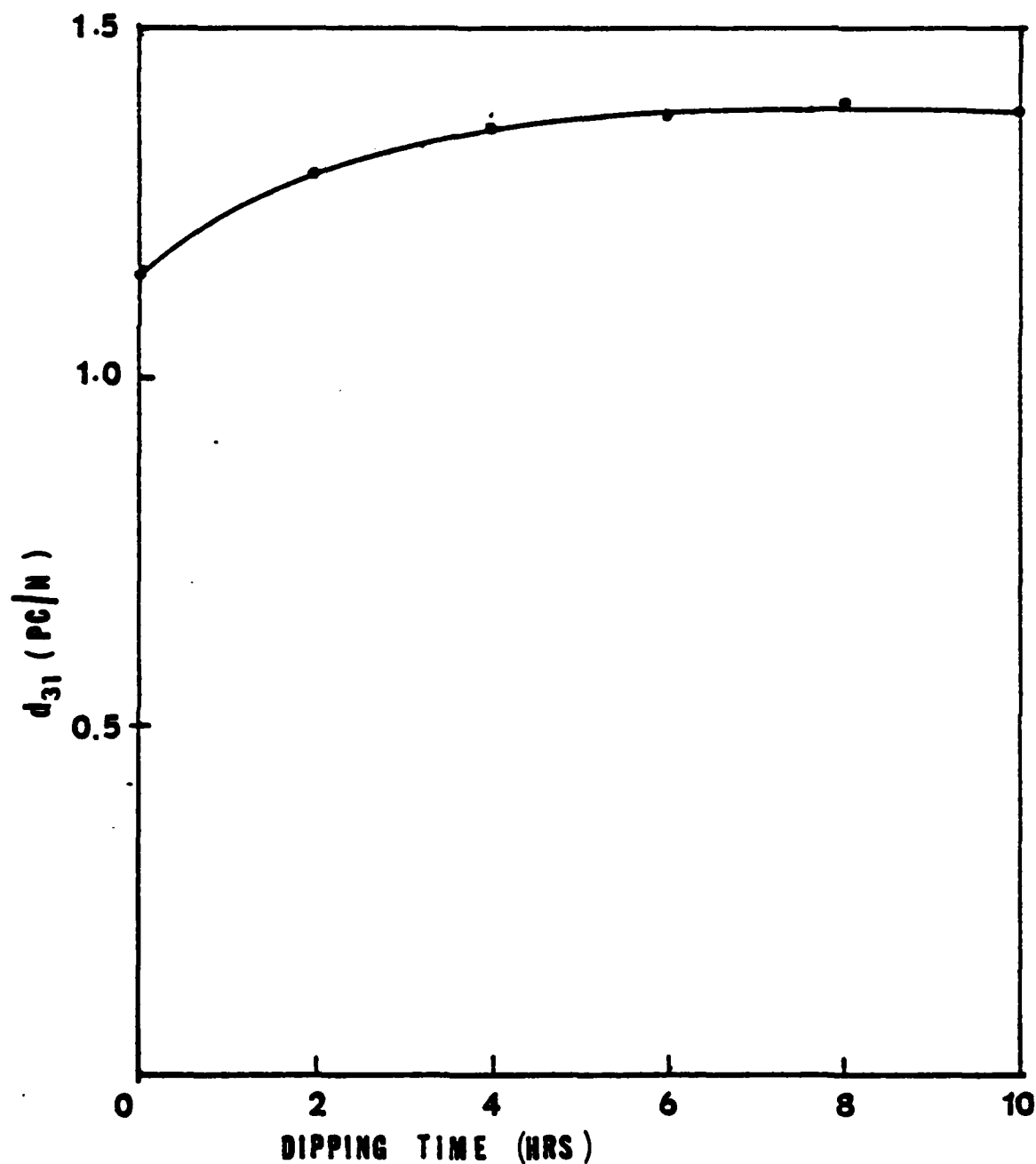


Fig. 1 - PIEZOELECTRIC STRAIN CONSTANT FOR UNORIENTED
POLED PVF₂ PLASTICISED FOR DIFFERENT TIMES

POLED AND THEN PLASTICISED

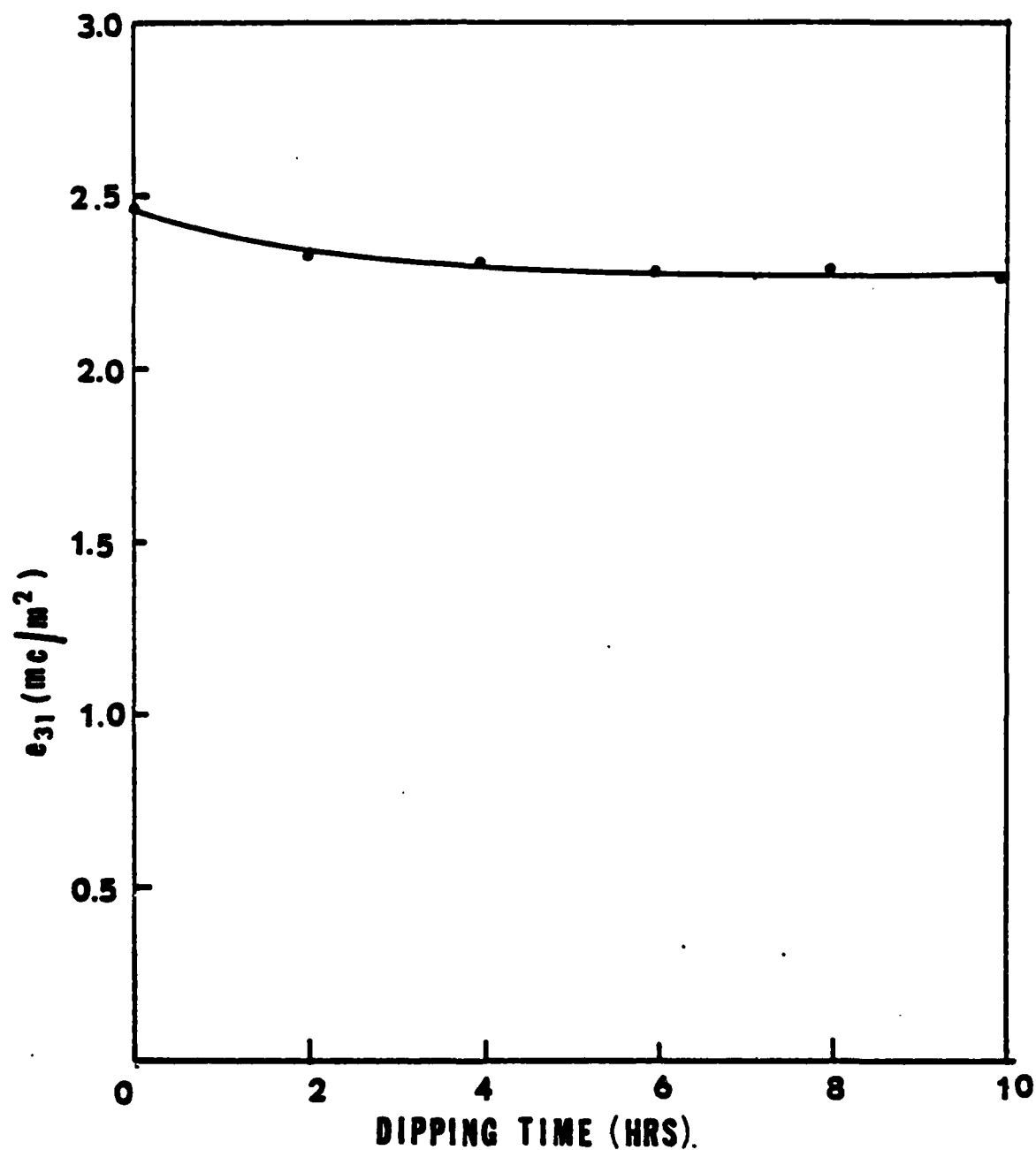


Fig. 2 - PIEZOELECTRIC STRESS CONSTANT FOR UNORIENTED
POLED PVF₂ PLASTICISED FOR DIFFERENT TIMES

POLED AND THEN PLASTICISED

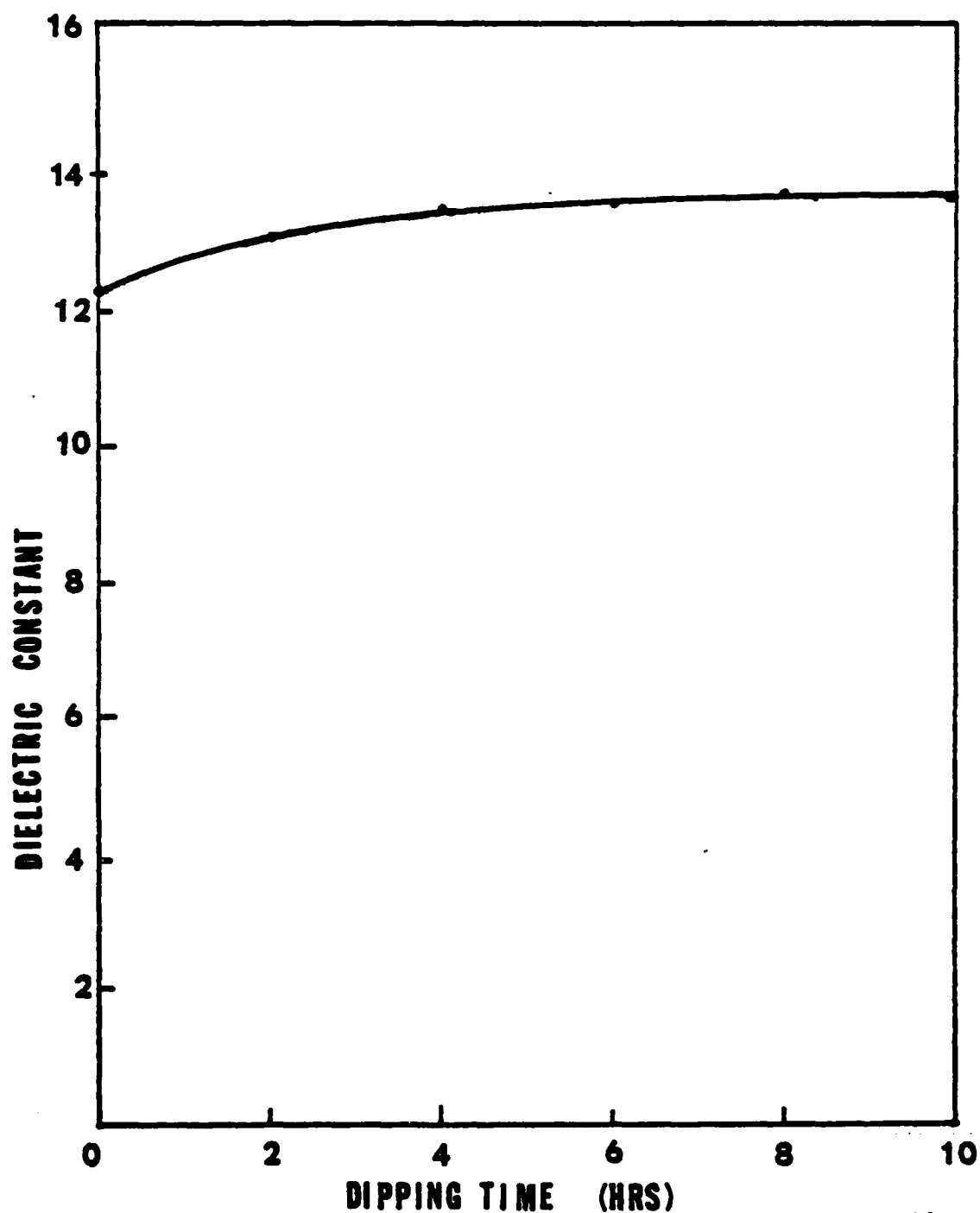


Fig. 3 - DIELECTRIC CONSTANT FOR UNORIENTED POLED PVF₂
PLASTICISED FOR DIFFERENT TIMES

POLED AND THEN PLASTICISED

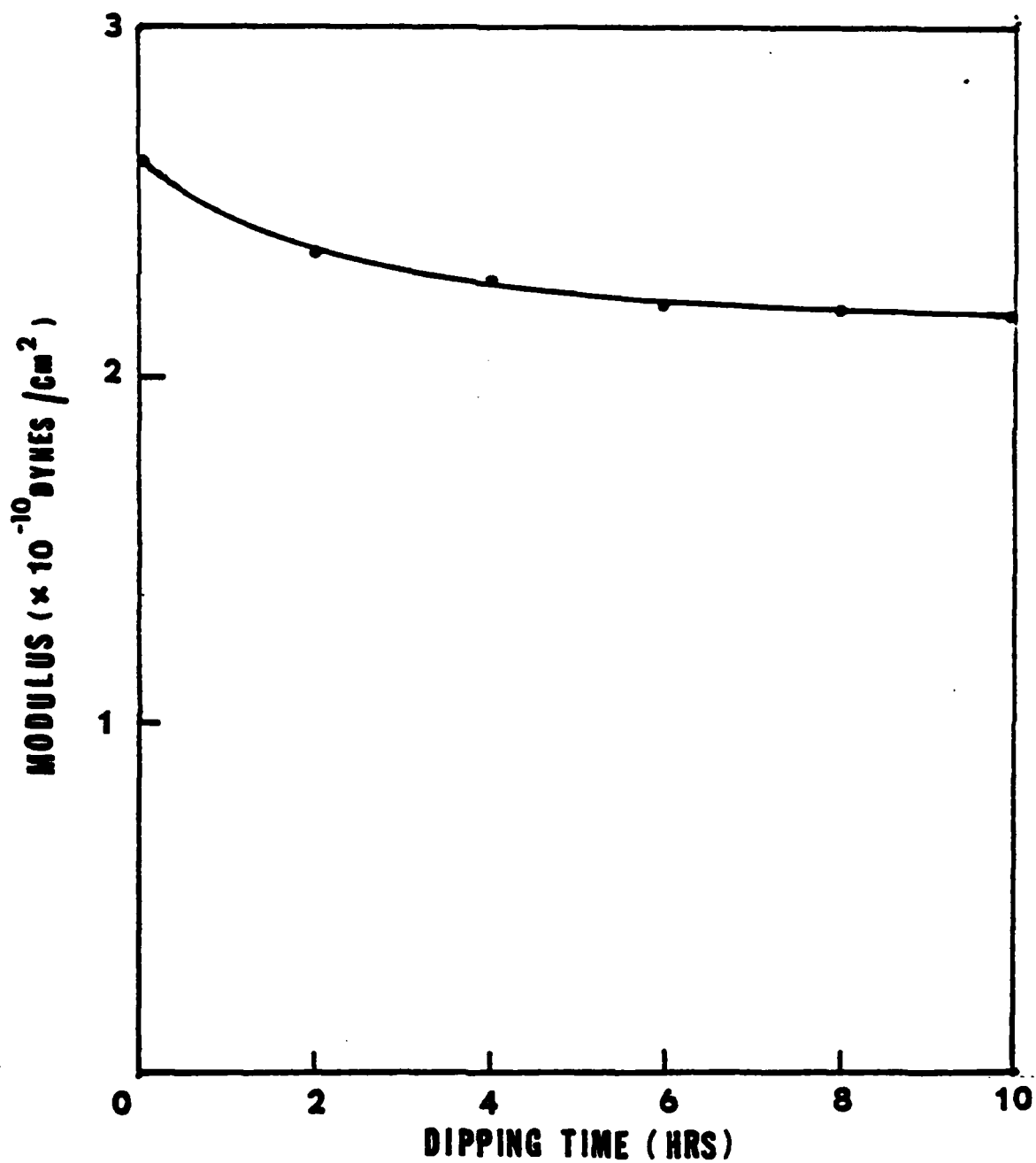


Fig. 4 - MODULUS FOR UNORIENTED POLED PVF_2
PLASTICISED FOR DIFFERENT TIMES

POLED AND THEN PLASTICISED

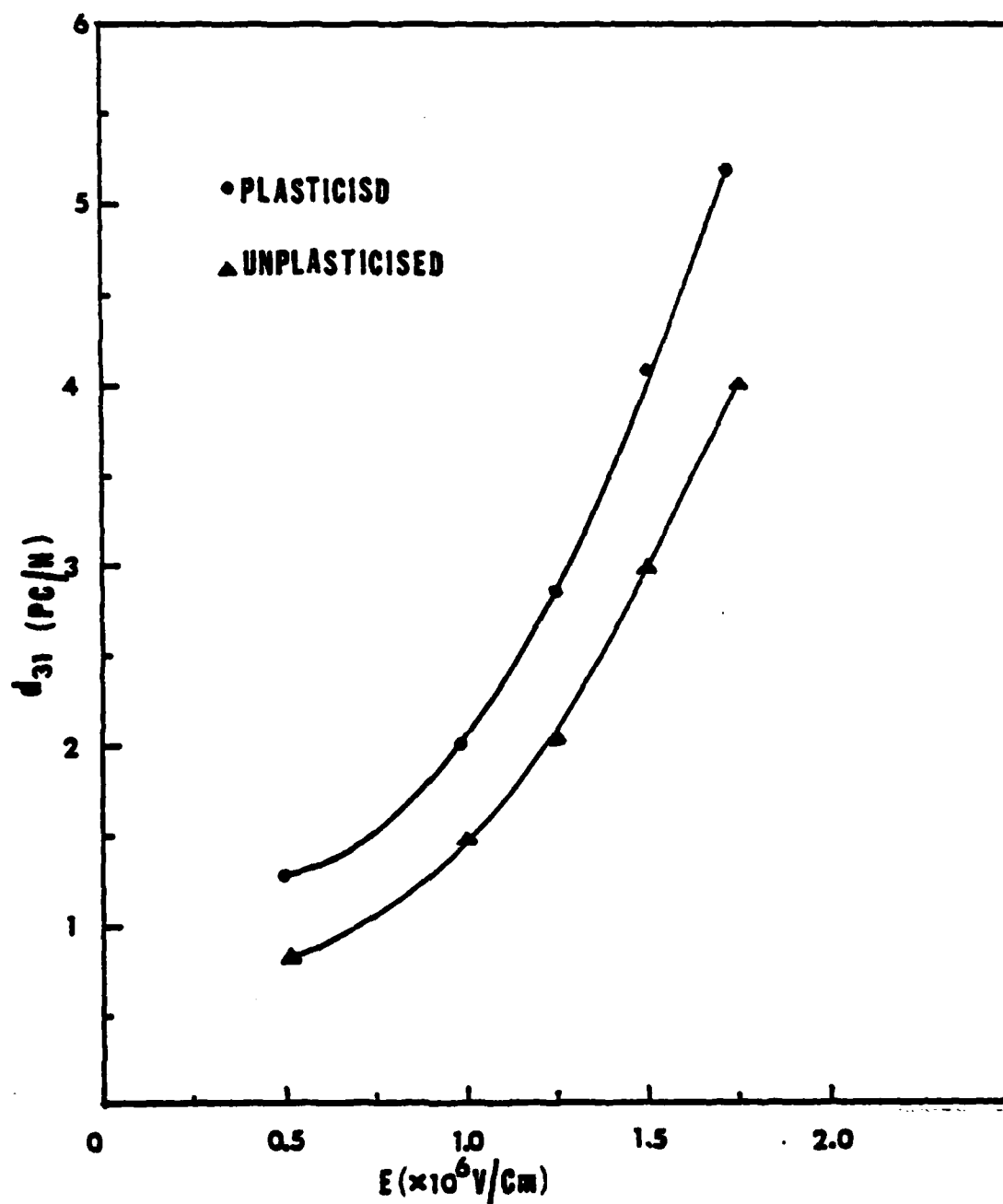


Fig. 5 - PIEZOELECTRIC STRAIN CONSTANT FOR UNORIENTED
PLASTICISED PVF₂ POLED AT DIFFERENT POLING FIELDS

PLASTICISED AND THEN POLED

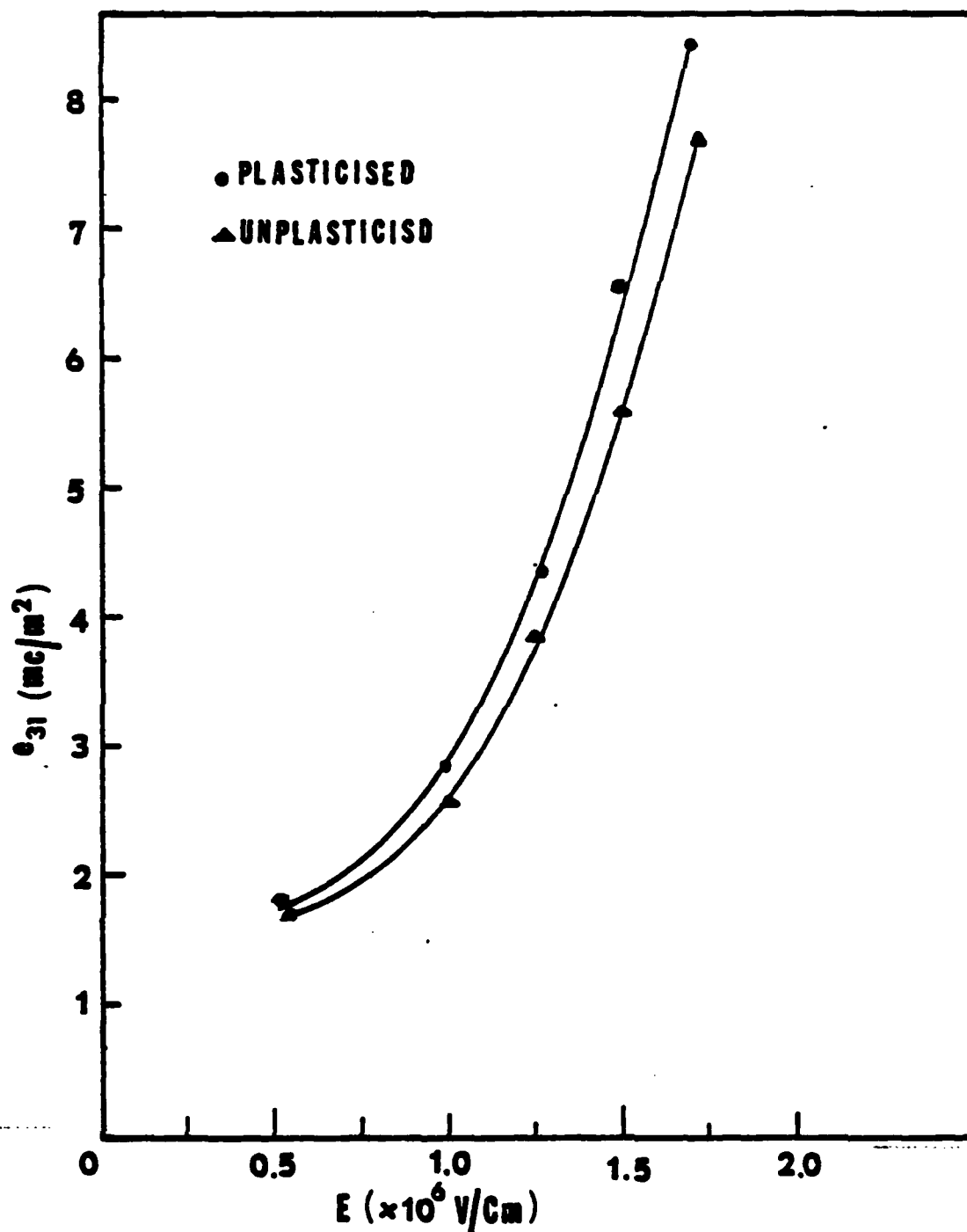


Fig. 6 - PIEZOELECTRIC STRESS CONSTANT FOR UNORIENTED
PLASTICISED PVF_2 POLED AT DIFFERENT POLING FIELDS

PLASTICISED AND THEN POLED

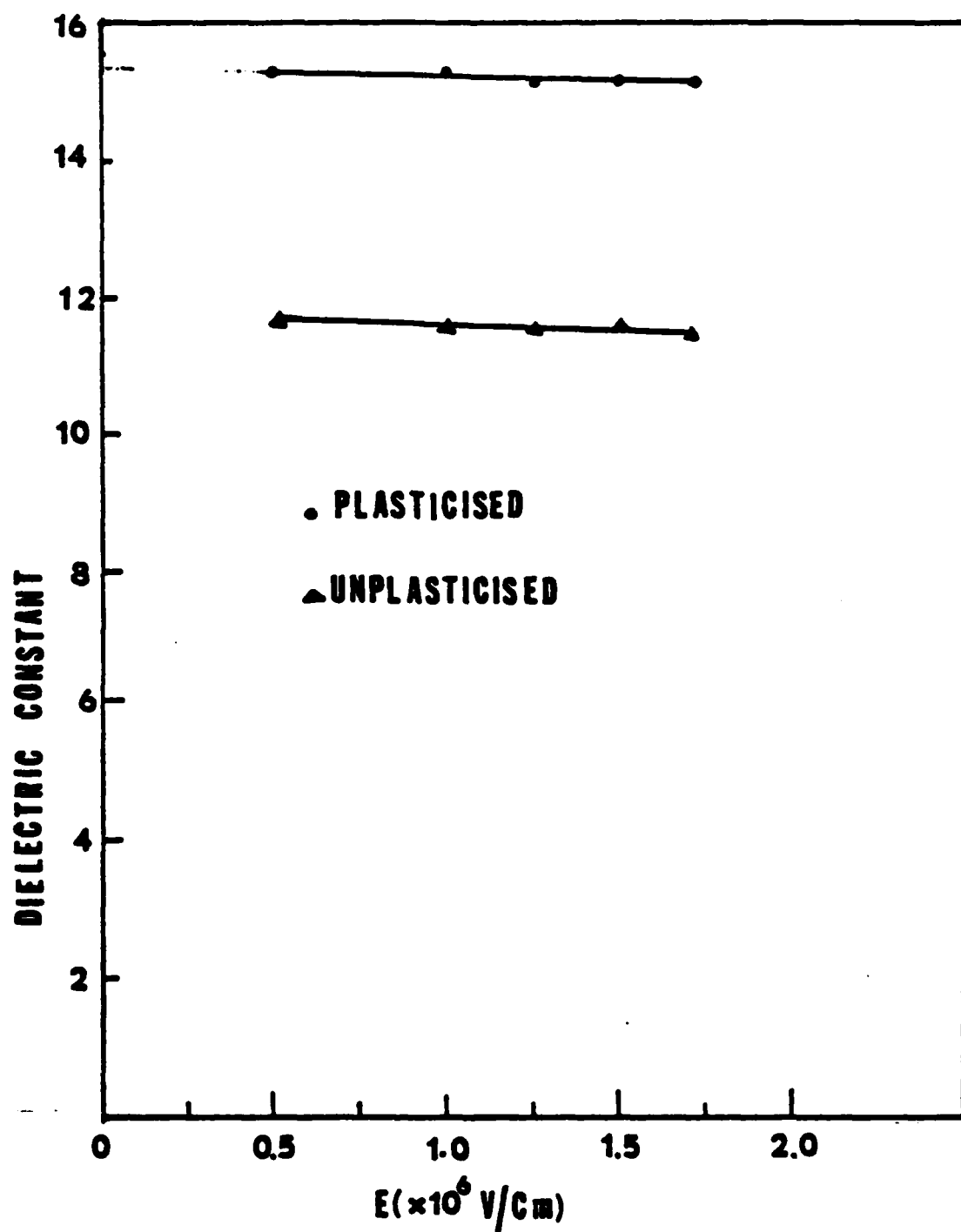


Fig. 7 - DIELECTRIC CONSTANT FOR UNORIENTED PLASTICISED
PVF₂ POLED AT DIFFERENT POLING FIELDS

PLASTICISED AND THEN POLED

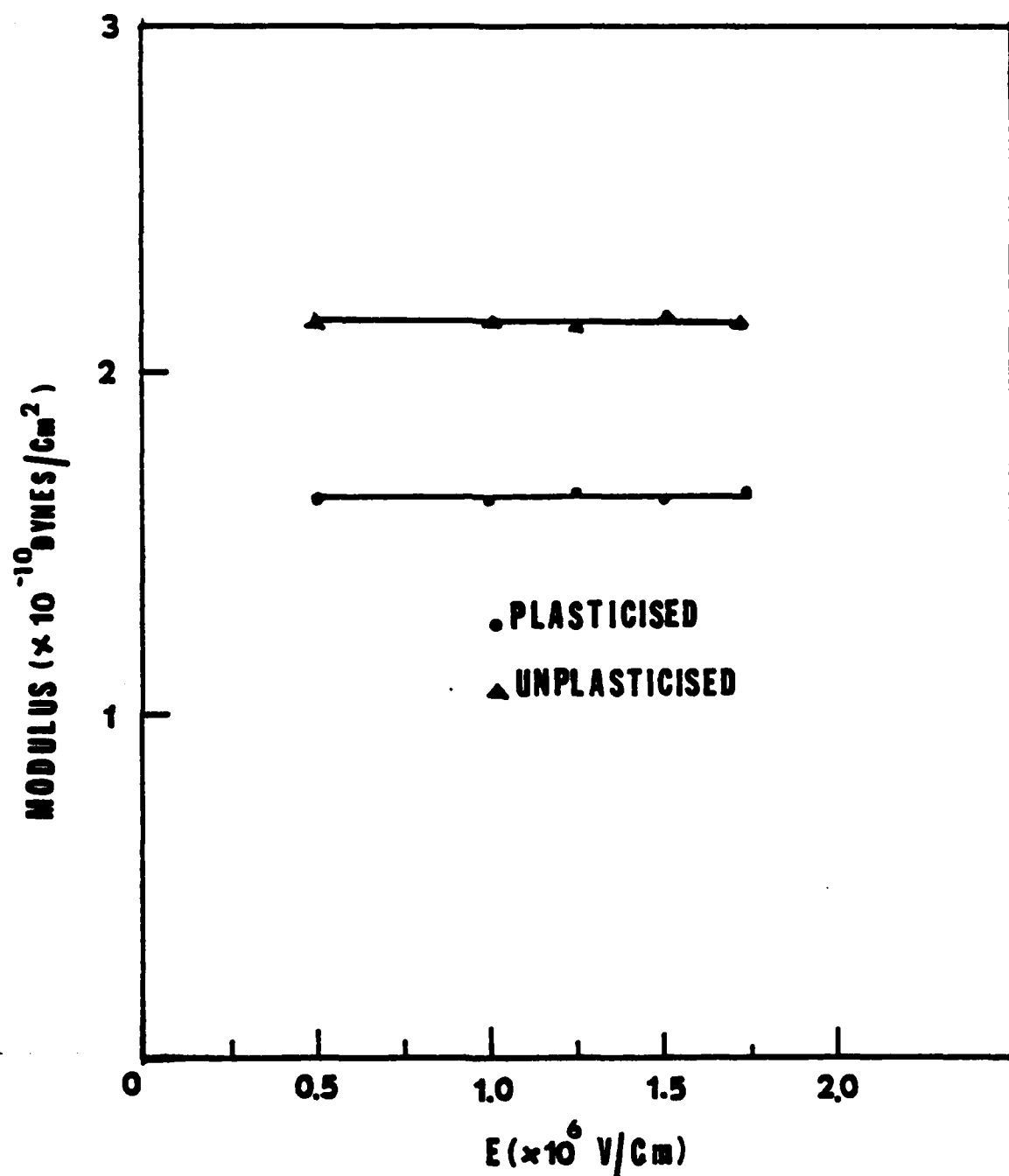


Fig. 8 - MODULUS FOR UNORIENTED PLASTICISED
PVF₂ POLED AT DIFFERENT POLING FIELDS

PLASTICISED AND THEN POLED

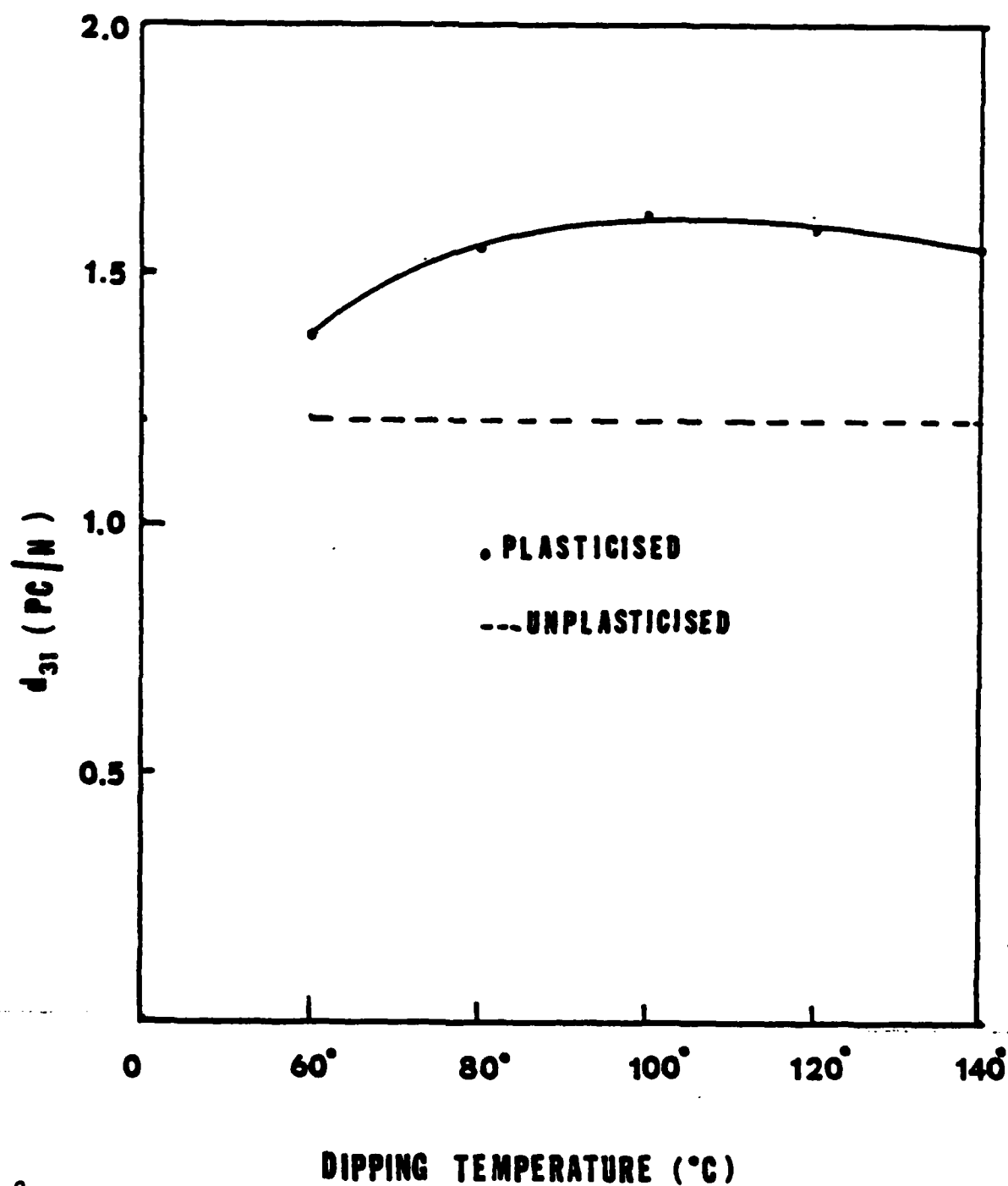


Fig. 9 -
 PIEZOELECTRIC STRAIN CONSTANT FOR UNORIENTED PLASTICISED P
 PLASTICISED FOR 8HRS AT DIFFERENT TEMPERATURES
 AND THEN POLED AT 1×10^6 V/Cm

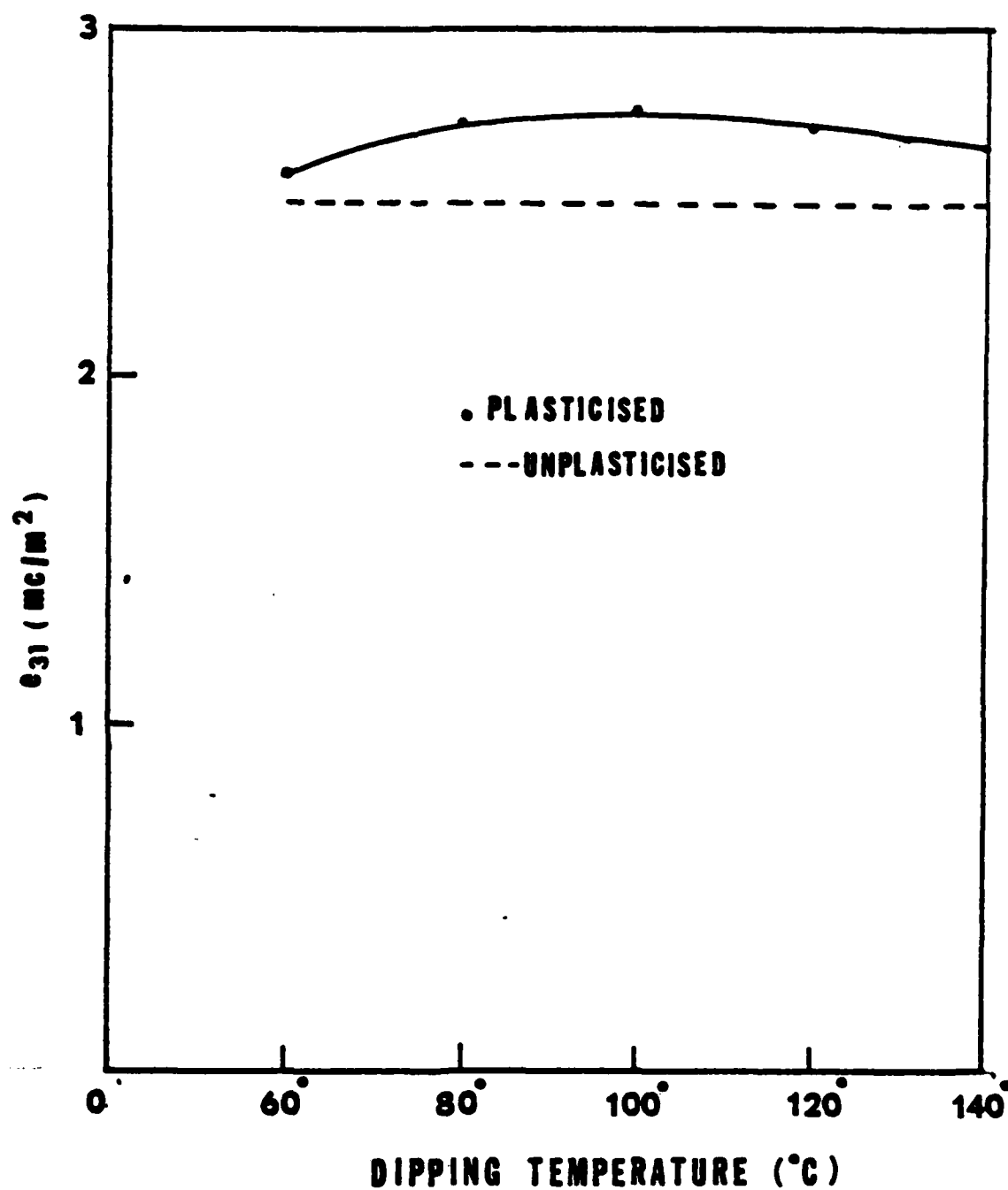


Fig. 10 -

PIEZOELECTRIC STRESS CONSTANT FOR UNORIENTED PLASTICISED P

PLASTICISED FOR 8 HRS AT DIFFERENT TEMPERATURES

AND THEN POLED AT 1×10^6 V/Cm

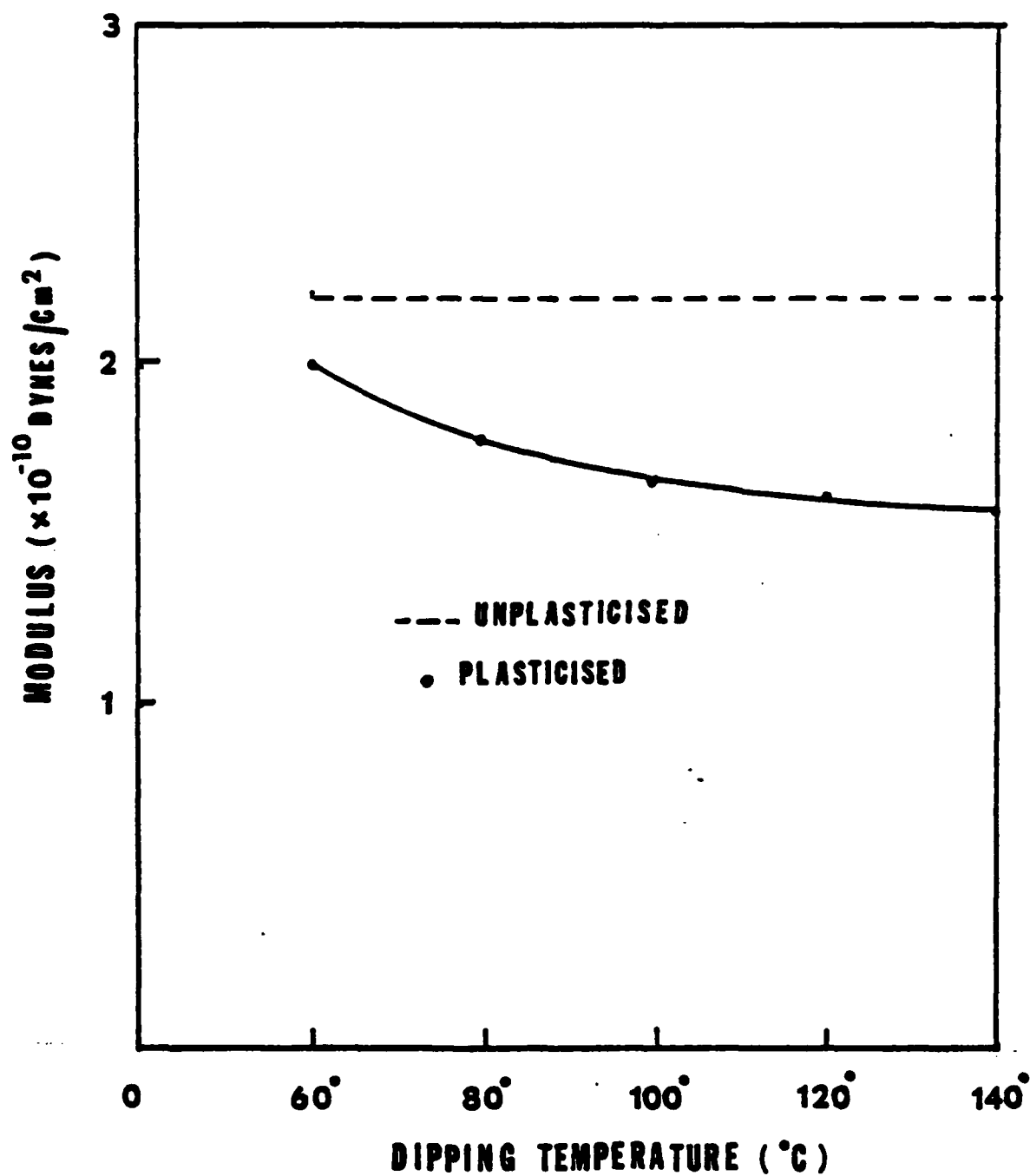


Fig. 11 - MODULUS FOR UNORIENTED PLASTICISED PVF₂
PLASTICISED FOR 8 HRS AT DIFFERENT TEMPERATURES
AND THEN POLED AT 1×10^6 V/Cm

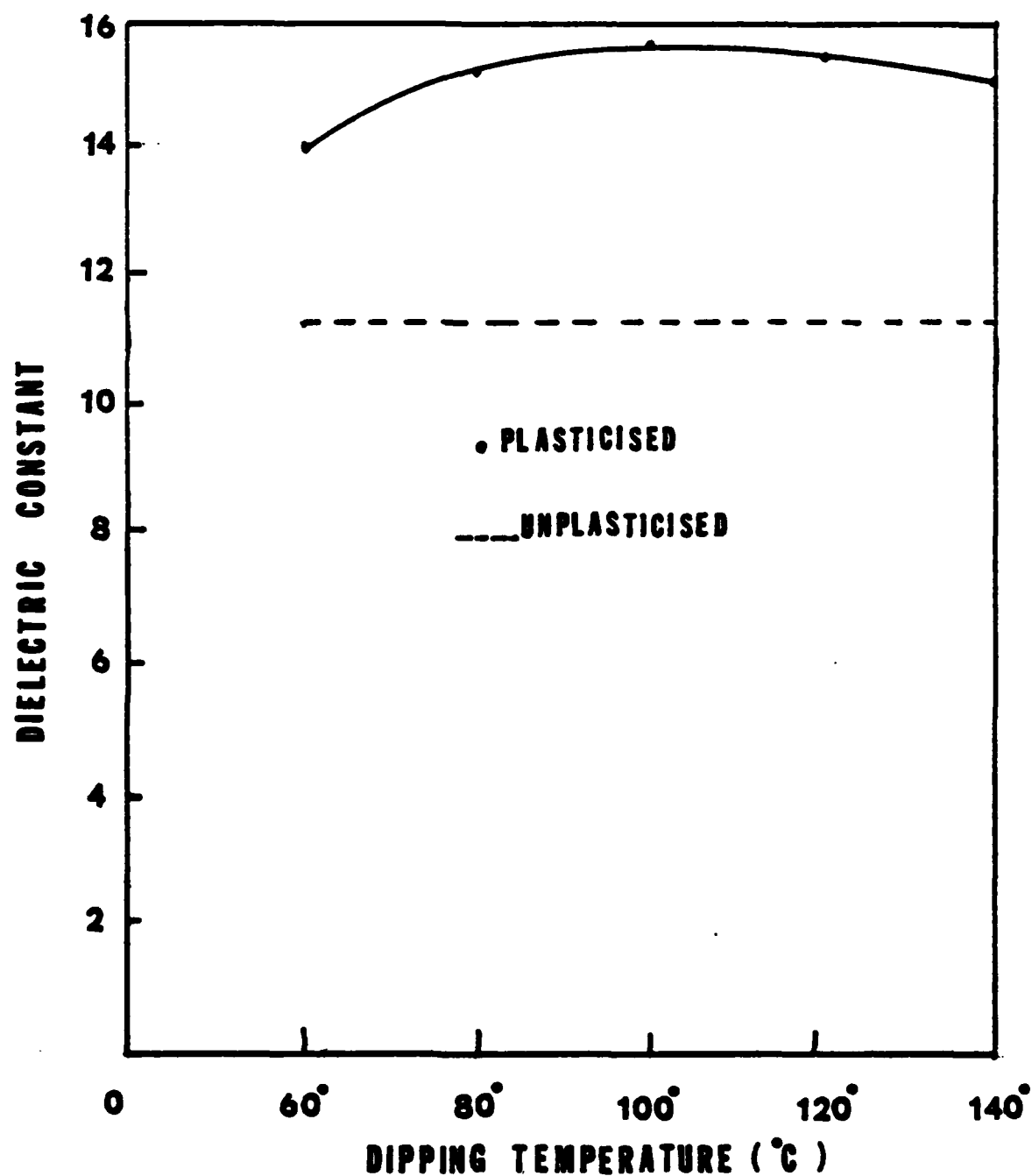


Fig. 12 - DIELECTRIC CONSTANT FOR UNORIENTED PLASTICISED PVF₂
PLASTICISED FOR 8 HRS AT DIFFERENT TEMPERATURES
AND THEN POLED AT 1×10^6 V/Cm

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